

KINETIC INHIBITION OF CO AND N₂ REDUCTION IN CIRCUMPLANETARY NEBULAE: IMPLICATIONS FOR SATELLITE COMPOSITION

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ABSTRACT

In contrast to the solar nebula, the conversion of CO to CH₄ and of N₂ to NH₃ in the circumplanetary nebulae of the Jovian planets is fast enough relative to radial mixing and nebula cooling rates that CO and N₂ are minor constituents in the circumplanetary nebulae. Thus, although the Jovian planets may have accreted carbon and nitrogen from the solar nebula mainly in the form of CO and N₂, these species were then reprocessed within the circumplanetary nebulae to form mainly CH₄ and NH₃. Satellites of the Jovian planets which accreted in sufficiently cool parts of their circumplanetary nebula are therefore predicted to retain large amounts of NH₃ and CH₄ in the form of clathrate hydrates and also very small but chemically important amounts of HCN.

Subject headings: molecular processes — planets: abundances — planets: general — planets: Jupiter — planets: satellites

I. INTRODUCTION

In a recent paper Lewis and Prinn (1980) discussed the chemistry of the principal carbon and nitrogen compounds expected in the early solar nebula. They concluded that the rates of conversion of CO to CH₄ and N₂ to NH₃ were slow compared to the rates of nebular radial transport or nebular thermal evolution. Under these circumstances nitrogen and carbon are present throughout the nebula largely in the form N₂, CO, and CO₂—compounds which are thermodynamically stable only at high temperatures in the inner nebula. This study also deduced the implications of this predicted nonequilibrium composition for the outer nebula on the retention of carbon on the terrestrial planets, and on the bulk compositions of the Jovian planets, of their satellites, and of comets.

These latter deductions assumed that the condensed particles which accreted to form satellites were identical to those which accreted to form the parent planet. However, especially in the case of the massive Jovian planets, the process of planetary formation may have led to very different pressures and temperatures in the circumplanetary nebula in which the satellites formed than in the nearby bulk solar nebula. In particular, models for the evolution of Jovian type planets imply an early stellar-like epoch in which the planetary luminosity was several orders of magnitude larger than present (Bodenheimer 1974; Perri and Cameron 1974; Graboske *et al.* 1975; Pollack *et al.* 1976). This early stellar-like epoch and the existence of common patterns in the planetary system and the satellite systems of the Jovian planets suggest that these systems may have formed in separate

but analogous ways (Black 1971; Cameron 1973*a*; Cameron and Pollack 1976).

Of the theories for satellite formation which have been proposed (see, for example, Cameron 1977; De, Alfvén, and Arrhenius 1977; Safronov and Ruskol 1977), the one analogous to the theory for planetary formation utilized by Lewis and Prinn (1980) involves condensation and accretion of satellites in flattened spinning gaseous nebulae surrounding the protoplanets (Cameron 1977). Detailed models for the formation of the satellites of Jupiter and Saturn in such gaseous circumplanetary nebulae have been proposed (Pollack and Reynolds 1974; Cameron and Pollack 1976; Pollack *et al.* 1976; Prentice and ter Haar 1979). The physical conditions in these circumplanetary nebulae are sufficiently different from the nearby bulk solar nebula that they may modify those particular conclusions of Lewis and Prinn (1980) concerning satellite composition. In this paper we examine the chemistry of nitrogen and carbon in the hypothesized circumplanetary nebulae of Jovian-type protoplanets in order to demonstrate the extent of this modification.

II. CIRCUMPLANETARY NEBULA MODELS

Models for temperature profiles in the circumplanetary nebulae of the major planets are at a more rudimentary stage than those for the solar nebula. Temperatures have been estimated using simple radiative equilibrium energy-balance models in transparent nebulae for Jupiter (Pollack and Reynolds 1974; Fanale, Johnson, and Matson, 1977; Cameron and Pollack 1976; Pollack *et al.* 1976) and for Saturn (Pollack *et al.* 1976). For Jupiter

these studies suggest that water ice condensation at and beyond Callisto's orbit in the circumplanetary nebula first occurred after 0.2–2 million years of Jupiter's existence. As the luminosity of Jupiter decreased and the nebula cooled, the ice condensation region progressed inward toward Jupiter, reaching the orbit of Ganymede after 0.8–8 million years. The nebula dissipated, and satellite formation ended after 1.5–15 million years and before Europa or Io could accrete significant amounts of water ice. For an isobaric circum-Jovian nebula at a pressure of 10^{-1} bars (which is consistent with the observed masses of the satellites), the temperature of Io is ~ 380 K at the time water ice begins condensing at 240 K at Ganymede's orbit (Pollack *et al.* 1976). Thus we deduce the following radiative equilibrium temperature profile in the equatorial plane:

$$T \approx 240 \left(\frac{r}{15.1} \right)^{-0.5}, \quad (1)$$

where T is condensate temperature and r is Joviocentric distance in Jovian radii. In contrast, for an isobaric circum-Jovian nebula at a pressure of 10^{-6} bar (approximately the nearby solar nebula pressure), ice condenses at 160 K, and from Fanale *et al.* (1977) and Pollack and Reynolds (1974) we have

$$T \approx 160 \left(\frac{r}{15.1} \right)^{-0.5}. \quad (2)$$

Similar deductions can be made for Saturn. In particular, at the time water ice begins condensing at the orbit of ring B in an isobaric circum-Saturnian nebula at 0.1 bar pressure, we deduce from Pollack *et al.* (1976)

$$T \approx 240 \left(\frac{r}{1.8} \right)^{-0.5}, \quad (3)$$

where r is Saturniocentric distance in Saturn radii.

Temperatures have also been estimated taking into account convection in the circumplanetary nebula (Pollack *et al.* 1976; Prentice and ter Haar, 1979). In particular, Pollack *et al.* (1976) argue that the circumplanetary nebula may have been sufficiently opaque to have allowed convection rather than radiation to be the dominant mode for transport of heat from the planet's photosphere outward through the circumplanetary nebula. For the solar nebula, Lewis (1974) has shown that available composition and density data for the planets and satellites are incompatible with radiative equilibrium temperature profiles but compatible with convective isobaric, isopycnic, or adiabatic equilibrium temperature profiles such as those predicted in the models of Cameron and Pine (1973). In the latter models, temperature varies roughly inversely with heliocentric distance. Pollack *et al.* (1976) assumed a similar relationship between temperature and Joviocentric distance in their opaque convective model for circumplanetary nebulae. From their work we deduce for 0.1 bar isobaric convective models

$$T \approx 240 \left(\frac{r}{15.1} \right)^{-1} \quad (\text{Jupiter}), \quad (4)$$

$$T \approx 240 \left(\frac{r}{1.8} \right)^{-1} \quad (\text{Saturn}), \quad (5)$$

using the same criteria concerning ice condensation at Ganymede and ring B as used in deriving (1) and (3).

For the purposes of this paper, a precise temperature profile is not required. However, we do wish to place feasible limits on the ranges of density and temperature expected in circumplanetary nebulae. We have placed upper and lower limits on the density ρ in the inner Jovian nebula disc in the following way. The total mass of the four Galilean satellites is $\sim 3.9 \times 10^{26}$ g. We can confidently assume that these satellites are composed of water ice and material less volatile than water ice. From Lewis (1972) these species comprise $\sim 1.1\%$ by mass of a solar composition nebula. For the lower limit to the inner nebula mass we thus take $(3.9 \times 10^{26})/0.011 = 3.55 \times 10^{28}$ g; for the upper limit we take the mass of Jupiter (1.9×10^{30} g). This inner nebula mass is assumed to lie in the region between the orbits of Io and Callisto. Note that we intend our neglect of the very low water contents of Io and Europa in computing the nebula mass to offset roughly our omission of material contributed to the Galilean satellites from outside this latter region. For the density scale height h perpendicular to the equatorial plane, we use Cameron's (1978) formula for hydrostatic equilibrium in a nebula disc and assume T varies as r^{-1} to obtain $h = 0.12r$. If we also assume by analogy with the solar nebula that ρ varies as r^{-1} (Lewis 1974), then we have for density limits

$$\frac{2.8}{r^3} > \rho > \frac{0.052}{r^3} \quad (\text{g cm}^{-3}). \quad (6)$$

The demand for hydrostatic equilibrium strongly favors adiabatic over isobaric models. For adiabatic models

$$T \propto \rho^{R/C_v}, \quad (7)$$

where R is the gas constant and C_v the heat capacity at constant volume. Constraints on temperatures are determined by demanding that they be cool enough to condense ice or water at Ganymede but warm enough to prevent ice or water condensation at Europa. This does not of course preclude Europa from capturing a little ice or water from outside its orbit. Thus, using (6) and (7) and referring to Lewis (1972) for ice condensation conditions, we have the following extremes in temperature profiles:

$$\begin{aligned} 272 \left(\frac{15.1}{r} \right)^{3R/C_v} > T > 294 \left(\frac{9.47}{r} \right)^{3R/C_v}, \\ \text{(high density)} \\ 232 \left(\frac{15.1}{r} \right)^{3R/C_v} > T > 245 \left(\frac{9.47}{r} \right)^{3R/C_v}. \\ \text{(low density)} \end{aligned} \quad (8)$$

We note that profiles (1) and (4) of Pollack *et al.* (1976) lie within these extremes, but that profile (2) of Pollack and

Reynolds (1974) does not because the nebula density assumed in the latter paper lies well below our lower bound.

In our chemical composition calculations for the circum-Jovian nebula in the following sections we have adopted a "nominal" model. This convective, adiabatic model is defined by the equations

$$T = 450 \left(\frac{\rho}{8.82 \times 10^{-5}} \right)^{R/C_v}, \quad (9)$$

$$T = 450 \left(\frac{5.95}{r} \right)^{3.5R/(C_v+R)}. \quad (10)$$

This model, which lies very close to our low density extreme, has been found by Lewis (1980) to be appropriate for explaining the pattern in the bulk densities of the Galilean satellites. The principal conclusions in this paper are not qualitatively affected by our assumption of any one particular temperature profile within our extremes given in equation (8). The exponents in equations (8) and (10) are both of order unity and vary by only about 40% between 100 K and 2000 K.

We emphasize that the above temperature profiles are intended to represent roughly conditions at the time at which the last important reactions between gases and condensates occurred in the circumplanetary nebula.

Since the specific reaction chosen (ice or water condensation) is relatively simple, this time most likely corresponds to a time near the end of the nebula's existence rather than to the time for accretion of objects sufficiently large for their interiors to be chemically isolated from the nebula. This latter accretion time is however of great importance for many other gas-condensate reactions relevant to satellite composition and for determining the degree of heterogeneity of accreted satellites. We will return to this topic in later discussion.

III. GAS-PHASE COMPOSITION

The thermochemical equilibrium stability fields in pressure-temperature space for various species in a gas with solar elemental abundances are illustrated in Figure 1. Also illustrated are the adiabatic pressure-temperature profiles for the solar nebula model adopted by Lewis and Prinn (1980) and for present-day Jupiter, and Neptune models (Prinn and Barshay 1977; Prinn and Lewis 1973). It is readily seen that as we move toward the proto-Sun in the solar nebula or toward the centers of the Jovian planets, CO and N₂ become increasingly more stable relative to CH₄ and NH₃. However, while CO and N₂ become the dominant carbon and nitrogen species near the proto-Sun in the solar nebula, they remain minor species throughout the atmospheres of the Jovian planets.

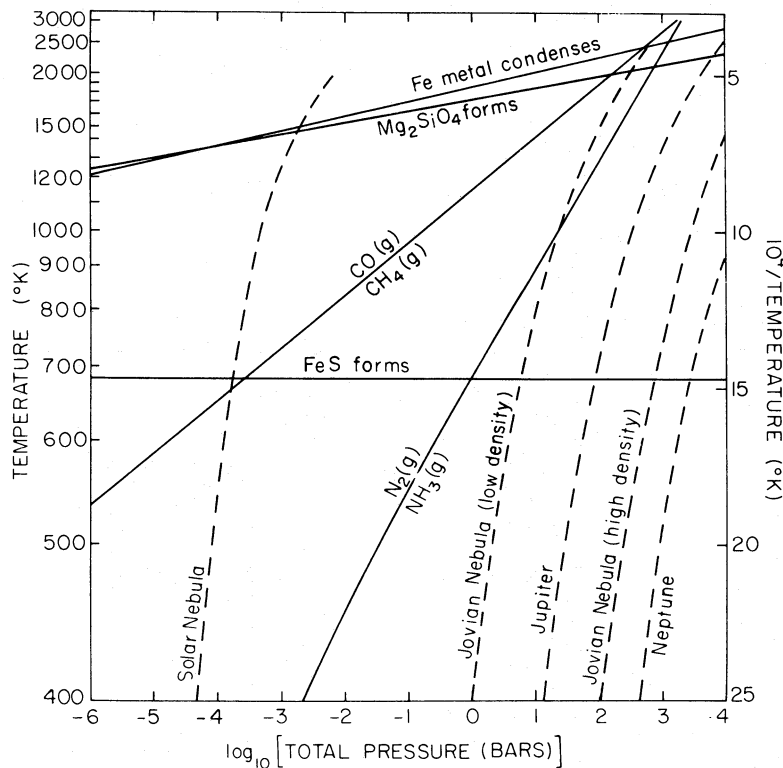


FIG. 1.—Some features of the equilibrium chemistry of a solar composition system as functions of temperature and pressure. The adiabats for models of the solar nebula; two extreme Jovian circumplanetary nebulae; and the present-day atmospheres of Jupiter and Neptune are illustrated in relation to the stability fields of Fe metal, Mg₂SiO₄ (forsterite), and FeS (troilite). The adiabat for our nominal model of the Jovian nebula is essentially identical to that denoted here as the low density extreme. The regions where CO or CH₄ and N₂ or NH₃ are the dominant carbon and nitrogen bearing gases, respectively, are also shown. The lines labelled CO-CH₄ and N₂-NH₃ denote boundaries where the abundances of the two gases are equal.

This important difference is illustrated more quantitatively and for a wider variety of compounds by comparing the detailed thermochemical equilibrium composition calculations for Jupiter (Prinn and Barshay 1977; Barshay and Lewis 1978; Fegley and Lewis 1979) with those for the solar nebula (Lewis and Prinn 1980; Fegley and Lewis 1980).

Also illustrated in Figure 1 are the adiabats for our nominal and extreme models of the circum-Jovian nebula as defined by equations (6)–(10). It is immediately apparent that conditions in the circum-Jovian nebula were much closer to those presently on Jupiter than to those in the nearby solar nebula. We therefore expect that conclusions concerning the compositions of the satellites of the major planets which are based on the composition of the nearby solar nebula rather than on the circumplanetary nebula may prove erroneous.

To illustrate the chemical equilibrium gas-phase composition of the circum-Jovian nebula, calculations were carried out over the temperature range 2000–100 K. The pressure-temperature profile in our nominal model defined by equations (9) and (10) was constructed stepwise using the heat capacity data for hydrogen and helium (Stull and Prophet 1971; Wagman *et al.* 1968) and assuming a solar H/He ratio. The heat capacities of the other gas molecules expected in a Jovian nebula with solar elemental abundances were ignored, since these other molecules comprise less than 1% by number of the nebula gases.

Solar elemental abundances were taken from Cameron (1973*b*). The assumed oxygen abundance was 80% of its solar abundance, since 20% of the oxygen was assumed to

be bound up in silicate and oxide minerals. Thermodynamic data for gases except ethane were taken from Stull and Prophet (1971) and Chase *et al.* (1974, 1975, 1978), while data for ethane were taken from Chao, Wilhoit, and Zwolinski (1973).

The calculated chemical equilibrium concentrations for the abundant nitrogen- and carbon-containing species are presented as functions of position in our circum-Jovian nebula model in Figures 2 and 3. At the orbital distance of Io in these calculations, NH_3 is $\sim 10^4$ times more abundant than N_2 , and CH_4 is respectively $\sim 10^{11}$ and $\sim 10^{16}$ times more abundant than C_2H_6 and CO. The abundance of N_2 becomes comparable to that of NH_3 at the orbit of Amalthea, while CO is comparable to CH_4 only at the surface of or within Jupiter itself.

However, rapid convection in the circum-Jovian nebula could enable N_2 and CO to be transported outwards from regions where they are abundant on a time scale shorter than that required for conversion of these species to NH_3 and CH_4 . This mechanism for producing nonequilibrium concentrations of species in atmospheres has already been quantitatively demonstrated for CO and N_2 on Jupiter (Prinn and Barshay 1977; Prinn and Olaguer 1981) and in the solar nebula (Lewis and Prinn 1980).

If N_2 or CO are present in a parcel of gas with mixing ratios in excess of those expected in equilibrium, they will be destroyed by conversion to their thermodynamically stable forms NH_3 and CH_4 at a rate which can be estimated from our knowledge of the kinetics of the rate determining reactions. The resultant quantitative expressions for gas-phase destruction times for CO and N_2 and

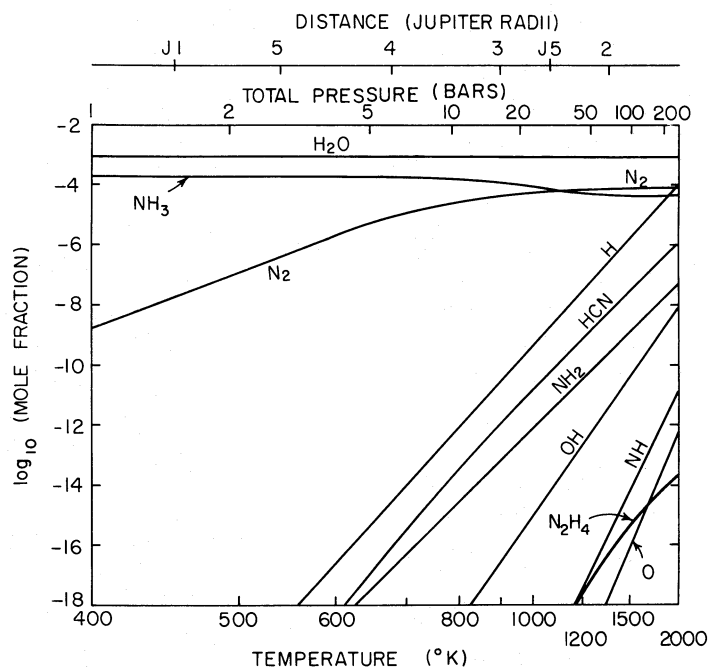


FIG. 2.—Equilibrium abundances of some oxygen- and nitrogen-containing gases in the equatorial plane of the nominal Jovian nebula model. The horizontal scales indicate temperature, pressure, and radial distance from the center of proto-Jupiter. The positions of Amalthea (J5) and Io (J1) are also indicated.

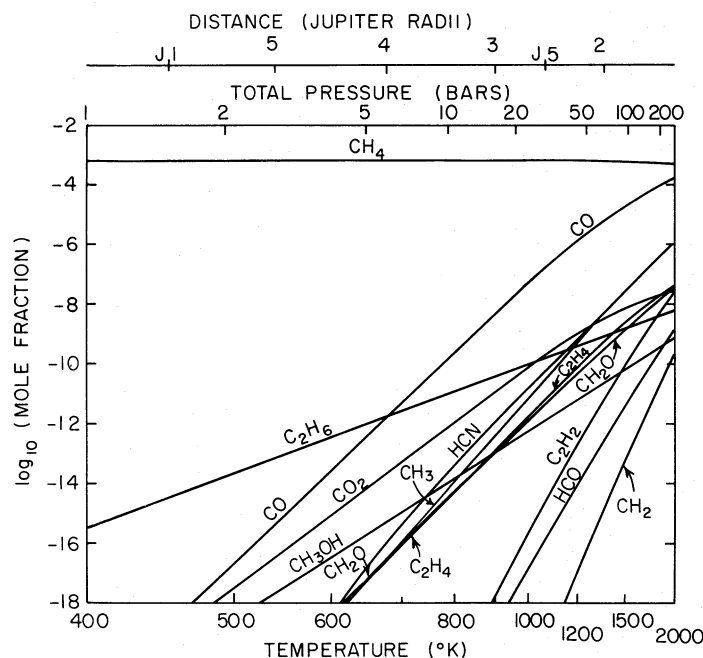
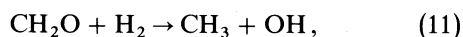
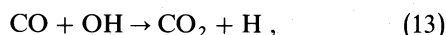


FIG. 3.—As in Figure 2 but for carbon-bearing gases

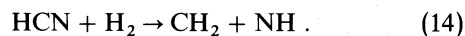
for metallic iron-catalyzed destruction of N_2 have been derived and discussed previously (Prinn and Barshay 1977; Lewis and Prinn 1980; Prinn and Olaguer 1981). The rate determining reactions for conversion of CO to CH_4 and N_2 to NH_3 in the gas phase are



and as discussed by Prinn and Barshay (1977) and Lewis and Prinn (1980) an equilibrium CO to CH_2O ratio is appropriate for computing the CO lifetime. For the gas phase conversion of CO to CO_2 the important reaction is



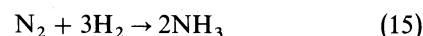
and we use the measured rate constant of this reaction (Baulch *et al.* 1976) and equilibrium OH concentrations (Prinn and Barshay 1977; Lewis and Prinn 1980) to deduce the conversion time of CO to CO_2 . Finally, for conversion of HCN to NH_3 we assume by analogy with equations (11) and (12) that the rate determining reaction is



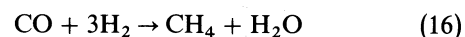
We deduce a rough estimate of the rate constant of this reaction by combining its equilibrium constant with the rate constant of the reverse reaction. The latter rate constant is assumed to be equal to the rate constant for the reverse of equation (12).

Metallic iron is present in thermochemical equilibrium in our nominal Jovian nebula model between 495 K and 2440 K. At higher temperatures it evaporates to Fe gas, and at lower temperatures it is converted totally to FeS and to Fe^{++} in silicates. The chemical lifetime for the

metallic iron-catalyzed conversion of N_2 to NH_3 by the net reaction



is inversely proportional to the surface area of the catalyst; that is, proportional to the radius of the metallic iron particles and inversely proportional to the metallic iron mass density in the Jovian nebula. For the particle radius we assume a nominal value of $100 \mu m$ based on studies of metallic iron in chondritic meteorites. We assume chemical equilibrium mass densities for metallic iron taking into full account the partial conversion of the metal to iron sulfide and silicates as the temperature in the Jovian nebula decreases toward 495 K. The rate of equation (15) is also weakly dependent on the NH_3 -to- H_2 ratio, and we assume chemical equilibrium for this ratio. The lifetime for the metallic iron-catalyzed reaction



could be crudely equated with that for reaction (15). However, carbonaceous material rather than CH_4 may be a more likely product of this reaction (Studier, Hayatsu, and Anders 1968). This material would tend to coat and deactivate the iron catalyst, as would coatings of other involatile materials on the grains. Such deactivation of the iron catalyst would increase lifetimes from those computed here. On the other hand, if particle radii are much smaller than $100 \mu m$, then shorter lifetimes would result.

The chemical lifetimes, t_{chem} , for the conversions represented by equations (11)–(15) are illustrated as functions of position in the Jovian nebula in Figures 4 and 5. Also

shown are the minimum radial mixing times in the Jovian nebula defined by

$$t_{\text{mix}} \geq l/v, \tag{17}$$

where l is the local radial pressure scale height in the nebula disc as defined by equations (9) and (10) and v is one-third of the local sound speed. The maximum mixing time is given by the lifetime of the circumplanetary nebula which is taken here as 10^{13} s = 0.3 million years. For producing nonequilibrium concentrations of species, rapid cooling of the entire Jovian nebula has the same effect as rapid radial mixing. The e -folding time for the decrease of temperature in the nebula is also assumed to be 0.3 million years (cf. Pollack *et al.* 1976).

For each chemical conversion of interest, we divide the circumplanetary nebula into an inner region where $t_{\text{chem}} < t_{\text{mix}}$ and an outer cooler region where $t_{\text{chem}} > t_{\text{mix}}$. In the inner region defined by $r < r^*$ the species involved in the chemical conversion are in chemical equilibrium. In the outer region ($r > r^*$) we define a "chemical scale height" h_{chem} (Prinn and Barshay 1977) such that air parcels moving radially outward a distance h_{chem} are chemically quenched. Provided h_{chem} is less than the

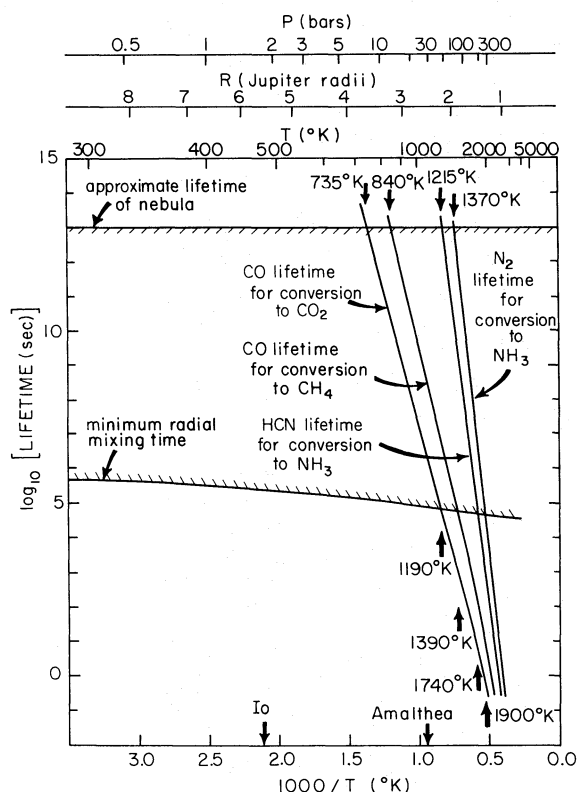


FIG. 4.—Lifetimes associated with four important gas phase chemical conversions in the equatorial plane of the nominal Jovian nebula model. The minimum and maximum quench temperatures deduced respectively for the maximum and minimum nebula mixing times are indicated for each conversion. The Jovian nebula pressure (P), temperature (T), and radial distances (R) scales and the positions of Amalthea and Io are also shown.

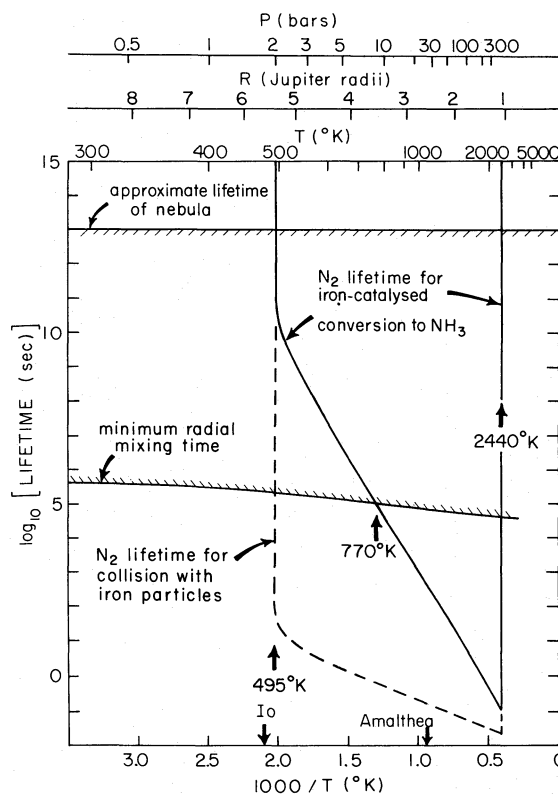


FIG. 5.—As in Figure 4 but for the iron-catalysed conversion of N_2 to NH_3 .

radial density scale height H , then the detailed solution for the continuity equation for the species being converted indicates that the mixing ratio of the species for $r > r^*$ is essentially equal to that at $r = r^*$. We refer to the radius r^* as the "quench radius" and to the temperature T^* at this radius as the "quench temperature."

For the chemical conversions illustrated in Figures 4 and 5 we find $h_{\text{chem}} \lesssim 15,000$ km while from equations (9) and (10) we deduce $H \gtrsim 40,000$ km. Thus the condition $h_{\text{chem}} < H$ discussed above is adequately met. From the upper and lower limits to the quench temperatures of the homogeneous conversions considered in Figure 4, we thus deduce the following upper and lower limits to species ratios in the outer circum-Jovian nebula:

$$1.6 < N_2:NH_3 < 1.8,$$

$$1.2 \times 10^{-6} < CO:CH_4 < 1.2 \times 10^{-2},$$

$$8.3 \times 10^{-4} < CO_2:CO < 7.9 \times 10^{-3},$$

$$1.9 \times 10^{-5} < HCN:NH_3 < 6.3 \times 10^{-3}.$$

If we assume iron catalysis is effective, then from Figure 5 the $N_2:NH_3$ and $CO:CH_4$ ratio limits are instead expressed by:

$$5.3 \times 10^{-4} < N_2:NH_3 < 0.14,$$

$$2 \times 10^{-14} < CO:CH_4 < 10^{-7}.$$

These ratios are markedly different from those in the nearby bulk solar nebula. In particular we have from Lewis and Prinn (1980) in the vicinity of Jupiter

$$80 < \text{N}_2:\text{NH}_3 < 5000$$

$$8 \times 10^{-4} < \text{CO}:\text{CH}_4 < 20,000,$$

when iron catalysis is effective. Thus although Jupiter may have been accreting carbon and nitrogen from the surrounding solar nebula mainly in the form of CO and N₂, these species were then reprocessed within the warmer circum-Jovian nebula to form mainly CH₄ and NH₃. This conclusion is appropriate for all but the maximum mixing time case discussed earlier which in essence corresponds to no mixing. In this case the species in the outer parts of the circum-Jovian nebula may have been accreted from the solar nebula but not subsequently mixed inwards to warmer regions where they could be effectively reprocessed. In this case (but only in this case) the results of Lewis and Prinn (1980), rather than the results presented here, would be applicable to the regular satellites of the outer planets.

IV. CONDENSED-PHASE COMPOSITION

We have carried out calculations using our nominal Jovian nebula model to determine which condensates are available in the nebula for accretion into satellites. A list of the condensates considered together with references for their thermodynamic properties is given in Table 1. For the gas-phase composition, we have used the results for the two extreme mixing times discussed in the previous section. We assume that iron-catalysed conversion of N₂ to NH₃ is effective. However, the potential for

TABLE 1
THERMODYNAMIC DATA SOURCES

Condensate	Reference
H ₂ O(s)	1
NH ₃ (s)	2
N ₂ (s)	3
CO ₂ (s)	4
CO(s)	5
CH ₄ (s)	1
NH ₃ ·H ₂ O(s)	6
2NH ₃ ·H ₂ O(s)	6
N ₂ ·7H ₂ O(s)	7
CO ₂ ·XH ₂ O(s)	7, 9
CO·7H ₂ O(s)	8
CH ₄ ·7H ₂ O(s)	7, 9, 10
NH ₄ HCO ₃ (s)	11, 12
NH ₄ CO ₂ NH ₂ (s)	11, 13
NH ₄ CN(s)	1
HCN(s)	1

REFERENCES.—(1) Weast 1969. (2) Overstreet and Giauque 1937. (3) Giauque and Clayton 1933. (4) Giauque and Egan 1937. (5) Clayton and Giauque 1932. (6) Weidenschilling and Lewis 1973. (7) Miller 1961. (8) Miller 1961 equation for N₂·7H₂O(s). (9) Davidson 1973. (10) Delsemme and Wenger 1970. (11) Wagman *et al.* 1968. (12) Kelley and Anderson 1935. (13) Egan, Potts, and Potts 1946.

TABLE 2
LOW TEMPERATURE CONDENSATES

CONDENSATE	T (K)	
	No Mixing	Maximum Mixing
H ₂ O(s)	235	235
NH ₄ HCO ₃ (s)	168	190
NH ₄ CO ₂ NH ₂ (s) ^a	173	188
NH ₃ ·H ₂ O(s)	160	159
HCN(s)	110	130
CH ₄ ·7H ₂ O(s)	94	94
N ₂ ·7H ₂ O(s)	48	60
CO·7H ₂ O(s)	41	57
CH ₄ (s)	41	41
N ₂ (s) ^a	16	19
CO(s) ^a	15	21

^a See text.

iron-catalyzed conversion of CO to CH₄ is ignored, since gas phase reactions alone are sufficient to make CO and CO₂ minor species relative to CH₄. Our study utilizes the "equilibrium accretion sequence" (Lewis 1972) in which the accretion of grains and cooling of the nebula are slow compared to gas-condensate reaction rates so that chemical equilibrium between grains and gas is attained at all times. In the alternate model, the "disequilibrium accretion sequence," accretion and cooling are fast relative to gas-condensate reaction rates so that a condensate once formed becomes effectively removed from the system.

The predicted condensates are listed in Table 2. Several comments on these results are necessary. First, although both NH₄HCO₃(s) and NH₄CO₂NH₂(s) are included in Table 2, the formation of one will consume all available CO₂(g) and prevent the formation of the other. However, both compounds are listed because of the similarity of their condensation temperatures, the possibility of slow attainment of equilibrium at low temperatures, and the uncertainties in the thermodynamic data. Second, N₂·7H₂O(s) and CO·7H₂O(s) are listed, although mass balance considerations indicate no free H₂O at their formation temperature. By this point all water is in the form of NH₃·H₂O and CH₄·7H₂O with none left to form the N₂ and CO clathrate hydrates. However, if formation of the methane hydrate is incomplete, water will be available to form these hydrates. Third, by the same argument, formation of N₂·7H₂O(s) and CO·7H₂O(s) may be incomplete and N₂(s) and CO(s) may form.

The predicted mass fractions of the condensed materials in the circum-Jovian nebula at low temperatures are illustrated in Figures 6 and 7. Condensation of hydrogen and the inert gases is not considered in these calculations. Figure 6 shows the mass fractions of the most abundant condensates. The material denoted as "rock" in this figure consists of 21.6% by weight troilite, 12.9% tremolite, 1.5% anorthite, 2.5% millerite, 14.6% magnetite, 43.9% serpentine, and 3% feldspar plus nepheline. These

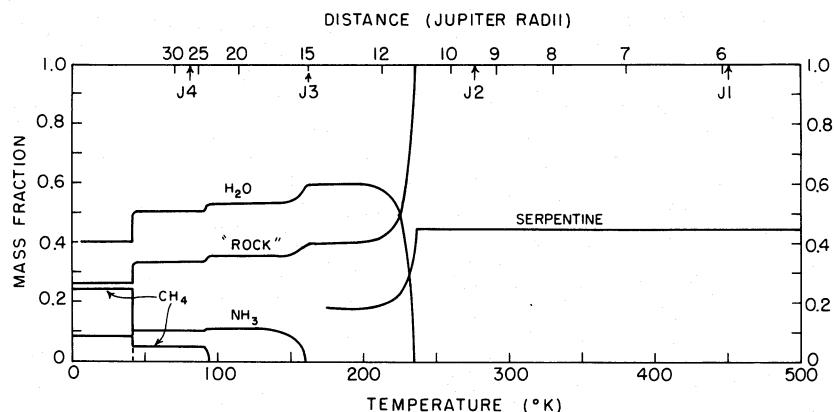


FIG. 6.—Abundances of the major components of condensed material in the equatorial plane of the nominal Jovian nebula model. The results assume no radial mixing. The total of silicates and other metal-bearing phases is designated "rock." Outgassing of a satellite containing hydrous silicates (e.g., serpentine) could produce surface ice but not the low bulk density associated with an ice-rich satellite. Temperature and radial distance scales in the Jovian nebula and the positions of Io (J1), Europa (J2), Ganymede (J3), and Callisto (J4) are indicated. In practice the temperatures in the outer part of the Jovian nebula (e.g., at Callisto) are expected to be similar to those in the surrounding solar nebula (e.g., 120 K).

results are for the no mixing case. Results for the maximum mixing case which are not illustrated are similar. In particular, the mass fraction of NH_3 drops slightly (to ~ 0.06) but the mass fractions of rock, H_2O , and CH_4 are essentially unchanged. The abundances of CO , CO_2 , N_2 , and HCN -containing condensates are illustrated in Figure 7. The lines labelled N_2 and CO are for the condensation of these gases as clathrate hydrates.

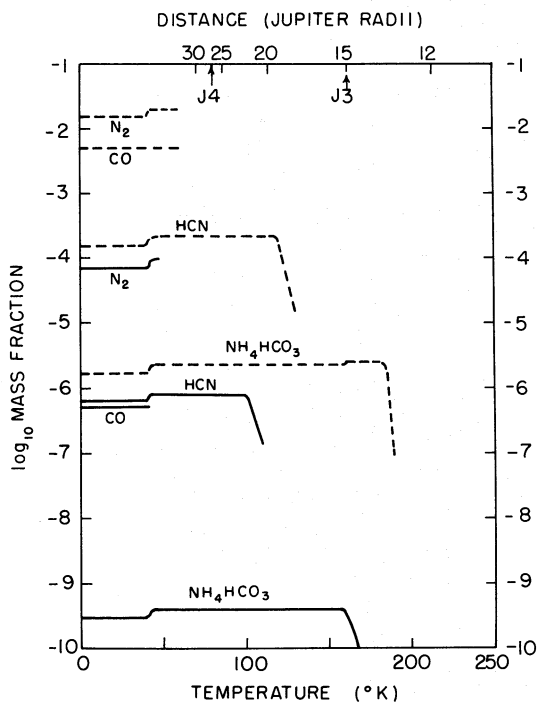


FIG. 7.—As in Figure 6 but for the abundances of several minor carbon- and nitrogen-containing species. *Solid lines*: results assuming no radial mixing; *dashed lines*: results assuming maximum radial mixing. As noted in Figure 6, temperatures at Callisto below about 120 K are not expected in actuality.

However, the graphed mass fractions refer only to the masses of N_2 and CO in the condensed material. The lines labeled NH_4HCO_3 represent the abundance of ammonium bicarbonate. However, if ammonium carbamate ($\text{NH}_4\text{CO}_2\text{NH}_2$) forms instead of NH_4HCO_3 , these lines also describe the abundance of the former condensate, although the condensation temperatures will be slightly different (see Table 2).

In contrast to the conclusions of Lewis and Prinn (1980), we find that retention of significant amounts of NH_3 as $\text{NH}_3 \cdot \text{H}_2\text{O}(\text{s})$ and of CH_4 as $\text{CH}_4 \cdot 7\text{H}_2\text{O}(\text{s})$, and $\text{CH}_4(\text{s})$ will occur in material condensed at sufficiently low temperatures. These condensates are expected to play important roles in the thermal evolution and present day internal structure of icy satellites (Consolmagno and Lewis 1978). Retention of nitrogen and carbon as $\text{NH}_4\text{HCO}_3(\text{s})$ and $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s})$ is predicted to be negligible due to the small CO_2 mixing ratio ($\leq 10^{-8}$) in the circum-Jovian nebula. Other condensates of disequilibrium gases such as $\text{HCN}(\text{s})$, $\text{N}_2 \cdot 7\text{H}_2\text{O}(\text{s})$, $\text{CO} \cdot 7\text{H}_2\text{O}(\text{s})$, $\text{N}_2(\text{s})$, and $\text{CO}(\text{s})$ are also predicted to be minor phases for nitrogen and carbon retention. For example, in the maximum mixing case the mass fractions of N_2 , CO , and HCN are 0.015, 0.005 and 0.0002 respectively, after complete condensation of these species as either clathrate hydrates or pure solids. We should emphasize, however, that HCN even at these low predicted abundances could be extremely important as a starting material for the production of more complex organic compounds in the atmosphere of an icy satellite such as Titan.

In applying these calculations to specific satellites, we emphasize that we have allowed the circumplanetary nebula temperatures to decrease continuously outward according to equation (10) in order to illustrate the complete condensation sequence. In practice, the circumplanetary nebula will presumably become isothermal in its outer parts as it blends into the surrounding solar nebula. Typical temperatures predicted in the solar

nebula at the distances of Jupiter and Saturn exceed 120 K and 60 K, respectively. Thus retention of CH_4 is not expected on Callisto but is expected on Titan.

Our results bear some resemblance to those obtained in low temperature condensation in a solar nebula in which chemical equilibrium is assumed at all temperatures in the gas phase (Lewis 1972). This similarity is due to the fact that the dominant carbon and nitrogen species are CH_4 and NH_3 in both the latter solar nebula model and in our gas-phase disequilibrium circum-Jovian nebula model. However, the similarity is not as important as it might first appear since the arguments presented by Lewis and Prinn (1980) tend to rule out gas-phase chemical equilibrium in the solar nebula at low temperatures as a viable hypothesis.

A disequilibrium accretion sequence applied to low temperature condensation in our circum-Jovian nebula model would yield somewhat different results from those presented in Table 2 and Figures 6 and 7. In particular, in the disequilibrium accretion sequence NH_3 is first retained as $\text{NH}_4\text{SH}(s)$ and then $\text{NH}_3(s)$ while CH_4 is not retained until $\text{CH}_4(s)$ condenses. Appreciable amounts of N_2 and CO would be retained only by condensation of their pure solids at temperatures below 20 K. Because of the similarities in gas phase composition noted in the previous paragraph, the results for the disequilibrium accretion sequence deduced by Lewis (1972) can be qualitatively applied to the gas-phase disequilibrium circum-Jovian nebula model considered in this paper.

V. CONCLUDING REMARKS

We have demonstrated in a nominal circum-Jovian nebula model that the mixing ratios of CO , CO_2 , and N_2 are low enough at the quench temperatures of their respective chemical reduction reactions for them to be minor species relative to CH_4 and NH_3 . Thus, as illustrated in Figure 6, perhaps Ganymede and certainly Callisto could have retained NH_3 as $\text{NH}_3 \cdot \text{H}_2\text{O}$. Retention of CH_4 as $\text{CH}_4 \cdot 7\text{H}_2\text{O}$ by Callisto is also possible but only in the unlikely circumstance that temperatures in the solar nebula surrounding Jupiter were as low as 94 K.

These conclusions can be contrasted to the predictions of Lewis and Prinn (1980) for the solar nebula in which

CO , CO_2 , and N_2 are the dominant carbon and nitrogen-containing species. If these latter predictions are correct, then we can surmise that Jupiter accreted carbon and nitrogen mainly as CO and N_2 but then reprocessed it to CH_4 and NH_3 . This reprocessing requires only that the lifetime of Jupiter's nebula exceed typical mixing times from the cool outer parts of the nebula into the warm inner parts where temperatures are above the chemical quench temperatures.

From Figure 1 it is evident that the Jovian nominal model adiabat (low density) we have chosen is as close to the solar nebula adiabat as one can justify for Jupiter's nebula. In addition, if Saturn also possessed a circumplanetary nebula, the minimum mass of this nebula would only be about 2.5 times less than the mass of our nominal Jovian nebula. Considering the fact that the rings show ice condensation occurred much closer to Saturn than to Jupiter, the Saturnian nebula adiabat is also expected to lie no closer to the solar nebula adiabat than our nominal Jovian adiabat. Thus, NH_3 and CH_4 are predicted to be equally or more stable in the Saturnian nebula than in our nominal Jovian nebula. Hence Titan is expected to have retained significant amounts of NH_3 (as $\text{NH}_3 \cdot \text{H}_2\text{O}$) and CH_4 (as $\text{CH}_4 \cdot 7\text{H}_2\text{O}$) and smaller amounts of HCN . If solar nebula temperatures at Saturn were equal to or even lower than 60 K, then retention of first N_2 (as $\text{N}_2 \cdot 7\text{H}_2\text{O}$) and then CO (as $\text{CO} \cdot 7\text{H}_2\text{O}$) is also possible.

Finally, we note that the predicted significant differences between circumplanetary nebulae and the solar nebula may enable the $\text{CO}_2:\text{CH}_4$ or the $\text{N}_2:\text{NH}_3$ ratios for example in an ice-rich body to be diagnostic of the formation region of the body. In particular, a CO_2 -rich comet or satellite is expected to have condensed in the solar nebula, but a CH_4 -rich comet or satellite is predicted to have formed in the circumplanetary nebula of its parent giant planet.

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